

[0016] FIG. 1 is a section through an electrochemical cell of the present invention; and

[0017] FIG. 2 shows an example of a multiple folded prismatic cell.

[0018] Referring to FIG. 1, the positive current collector 12, consists of aluminium or nickel foil, typically 15 microns thick, to which is bonded the active cathode 13. The most widely used material for the cathode is a lithiated intercalation compound such as LiCoO_2 , carbon black or graphite and a polymeric binder such as poly(vinylidene difluoride) PVDF. The main feature of this invention is the addition of the lithium salt of a sulphur oxy-acid to the cathode formulation. The additive may be chosen from one of a number of lithium sulphur oxy-acid salts, particularly lithium dithionite $\text{Li}_2\text{S}_2\text{O}_4$, or lithium sulphite Li_2SO_3 , added in a proportion of up to 10% by weight of cathode. The negative current collector 18, consists of nickel or copper foil, typically 12 microns thick, to which the anode material 17, consisting of meso carbon or graphite bound together with around 10% of a suitable polymer. The separator/electrolyte 15, interposed between the positive and negative electrodes, is typically around 75 microns thick and is prepared from a polymer having basic or tertiary nitrogen groups in its structure and an electrolyte salt both of which are dissolved in a common solvent. Suitable polymers include poly(vinyl pyridine), poly(vinylpyrrolidone) and thermally restructured poly(acrylonitrile). The electrolyte salt may be one or more chosen from LiAlCl_4 , LiBF_4 , LiPF_6 , LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{Li}(\text{F}_3\text{SO}_3)$. Other lithium salts which are preferably but not necessarily soluble in sulphur dioxide may be used as an implementation of this invention.

[0019] An electrochemical cell having the structure described above may take the form of a coin cell, a wound cylindrical cell or a multifolded prismatic format. The latter is preferred for large cells and supercapacitors. FIG. 2 shows an example of a multiple folded prismatic cell. The multiple folded prismatic cell comprises an anode 2, cathodes 4, cathode current collectors 6, and separators/electrolyte 8.

[0020] In order to facilitate a full and complete understanding of the present invention, reference will now be made to the following non-limiting Examples.

EXAMPLE I

[0021] A cathode was prepared by mixing together lithium cobalt oxide 77%, Super P carbon 6%, lithium dithionite 10% and PVDF binder 7%, all by weight. The binder was first dissolved in N-methyl pyrrolidone as a 4.5 w/v solution. The slurry was coated by doctor blade technique on to aluminium foil 15 microns thick. After solvent removal in an anhydrous atmosphere, the cathode was dried under vacuum at 105° C. for 8 hours. The separator/electrolyte was prepared by making up a solution of PVDF, poly(4-vinylpyridine) and LiAlCl_4 (1:2:3 weight ratio) in a mixture of dimethylformamide and N-methyl pyrrolidone. This solution was coated by doctor blade technique on to the previously prepared graphite anode already coated on to nickel foil. The solvents were removed by heating to 105° C. in a dry inert atmosphere for 1 to 2 hours. The anode/separator/

electrolyte and the cathode were then laminated together using steel rollers to make a cell as shown in FIG. 1.

EXAMPLE II

[0022] In this Example, the same cathode and anode as that of Example I were used with a different separator/electrolyte composition. The latter was prepared using anhydrous poly(vinylpyrrolidone) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved in a mixture of dimethylformamide and propylene carbonate. The solution was coated on to the anode as described in Example I, dried under vacuum to remove the solvents and then laminated on to the cathode.

EXAMPLE III

[0023] In this Example, the cathode was a composite of vanadium (IV) oxide V_2O_4 and lithium sulphite Li_2SO_3 in a 1:1 molar ratio. The cathode mix was prepared using 85% of this active material, 5% Super P carbon, 6% thermally restructured poly(acrylonitrile) and 4% PVDF binder. The procedure for preparation and coating of the paste were the same as in Example I. The separator/electrolyte was prepared using poly(acrylonitrile) thermally restructured at 250° C. under vacuum and LiAlCl_4 . These materials were dissolved in a mixture of N-methyl pyrrolidone and dimethylformamide. The solution was coated on to the anode as described in Example I, dried under vacuum to remove the solvents and then laminated on to the cathode.

EXAMPLE IV

[0024] In this Example, the cathode was prepared by mixing together lithium manganese (III, IV) oxide, LiMn_2O_4 (80%), lithium sulphite (9%), Super P carbon (6%) and PVDF binder (5%) as a 4.5 w/v solution in N-methyl pyrrolidone. The cathode mix was coated on to expanded nickel foil. The separator/electrolyte was prepared using poly(4-vinylpyridine) and LiAlCl_4 in dimethylformamide. This solution was coated on to the cathode which had previously had the carrier solvent removed under vacuum. Following a further drying operation, the composite cathode and separator/electrolyte was laminated to a lithium foil anode pressed on to a copper foil current collector.

[0025] The cells fabricated as described above were charged at a current density up to 0.2 mA/cm^2 , and a maximum voltage of 4.2V in laboratory cells having a pressure monitor. After allowing to stand for at least 3 days, the cells were cycled at a current density of 0.5 mA/cm^2 . Following repeated cycling at this higher rate, no excess pressure was generated in any of the cells tested. The conductivity of the original solid polymer electrolyte was observed to increase by a factor of between 10 and 30 fold on "in situ" generation of the sulphur oxides.

1. An electrochemical cell which comprises the following:

- (i) a positive electrode which, in addition to the cathodic active material, contains a compound MA_xO_y , where M is an alkali or alkaline earth metal and A is a non-metallic element where $0.3 < x \leq 2.0$ and $1.3 < y \leq 4.0$, such that on charging, the acid anhydride A_xO_y is generated "in situ", and
- (ii) a solid composite polymer film acting as separator whose structural units contain basic functional groups containing nitrogen atoms in 5 or 6 member heterocyclic rings or in tertiary aliphatic configuration into